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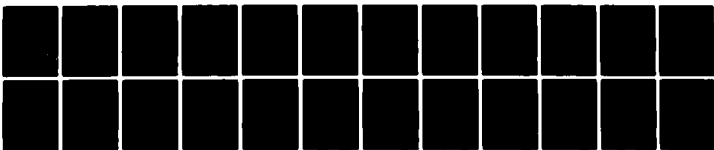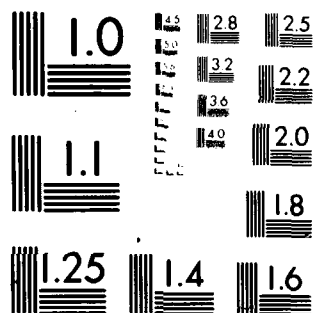MAY 80   M AKIYAMA, M H CHISHOLM, F A COTTON   N00024-76-C-0826
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THE TETRADECAISOPROPOXYDIHYDRIDOTETRATUNGSTEN STORY

by

M. Akiyama, M. H. Chisholm, F. A. Cotton, M. W. Extine,
D. A. Haitko, J. Leonelli, and D. Little

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Tetradecaisopropoxydihydridotetratungsten, $W_4(\mu-H)_2(OPr^i)_{14}$, has been isolated from the reaction between $W_2(NMe_2)_6$ ($M \equiv M$) and excess isopropanol and has been characterized by ir, nmr, mass spectroscopy and a single crystal X-ray study. The latter reveals a centrosymmetric molecule, $[W_2(\mu-H)(OPr^i)_7]_2$, having a chain of

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four tungsten atoms with two short, 2.446(1) Å, and one long, 3.407(1) Å, tungsten-to-tungsten distances. Each tungsten atom is coordinated to five oxygen atoms and a bridging hydride in a distorted octahedral geometry. The terminal tungsten atoms each have three terminal OPr^i ligands, but the internal tungsten atoms have only one which creates inequality in the formal oxidation states of the two types of tungsten atoms. Cryoscopic molecular weight determinations showed that the tetranuclear moiety is preserved in benzene, while in p-dioxane the molecule dissociates into two dinuclear fragments. NMR studies show that the molecule is fluxional on the nmr time scale: the seven crystallographically different OPr^i ligands are rapidly scrambled and the hydride ligand sees two equivalent (time averaged) tungsten atoms. The hydride resonance appears as a singlet at $\delta = 7.87$ ppm, flanked by satellites of roughly one fifth intensity due to coupling two tungsten - 183 nuclei (^{183}W, $I = \frac{1}{2}$, 14.4% natural abundance), $J_{^{183}W-^1H} = 96$ Hz. $W_4(\mu-H)_2(OPr^i)_{14}$ reacts with pyridine to form a Lewis base adduct or solvent compound $W_2(\mu-H)(OPr^i)_7(py)_x$, but does not eliminate Pr^iOH to give the known compound $W_2(OPr^i)_6(py)_2$. The bridging hydride ligand is not labile to exchange with the hydroxyl proton of Pr^iOH, but rapidly reacts with a number of unsaturated hydrocarbons (C_2H_4, $CH_2=C=CH_2$, 1-butene, $PhC\equiv CPh$) to give either products of M-H insertion or isomerization. Crystal data for $W_4(\mu-H)_2(OPr^i)_{14}$ are: a = 12.645(4), b = 13.157(4), c = 9.788(3) Å; α = 102.43(2), β = 67.80(2), γ = 101.05(2)°; V = 1461.5(7) Å^3; space group P$\bar{1}$.

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Introduction

Previously we have shown[2] that tungsten, unlike molybdenum, does not form an extensive series of dinuclear hexaalkoxides ($M \equiv M$). Indeed, only the extremely bulky tert-butoxy ligand gave a simple dinuclear compound, $W_2(OBu^t)_6$, in the alcoholysis reaction 1, and this was not thermally stable. The reaction involving isopropanol and pyridine as solvent gave

$$M_2(NMe_2)_6 + ROH(excess) \rightarrow M_2(OR)_6 + 6 HNMe_2$$
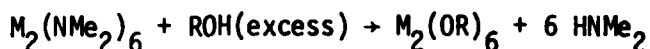
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where $M=Mo^3$, $R = Bu^t$, Pr^i, Me_3Si, Me_3CCH_2, $M=W^2$, $R=Bu^t$ only

$W_2(OPr^i)_6(py)_2$ which contained four coordinate tungsten atoms united by a triple bond. Tungsten showed a marked preference, relative to molybdenum, to increase its coordination number. In this paper, we show a further difference between tungsten and molybdenum, namely the ability and willingness of tungsten to undergo oxidation from the +3 to the +4 state under very mild conditions. A preliminary communication reporting some of this work has appeared.[4]

Results and Discussion

Synthesis. Addition of Pr^iOH (excess) to a hydrocarbon solution of $W_2(NMe_2)_6$ yields a dark solution which, upon stripping of the solvent, gives a black solid of empirical formula $W(OPr^i)_3$ based on elemental analyses. This black substance gave a very complex ^{1}H nmr spectrum and was thermally unstable yielding isopropanol, propylene and small quantities of a volatile crystalline tungsten isopropoxide, believed to be $W(O)(OPr^i)_4$.[5] From this

crude black product dissolved in hexane at <u>ca.</u> -15°C, black shining crystals, $W_4(\mu-H)_2(OPr^i)_{14}$, were obtained in approximately 50% yield based on tungsten.

The reaction between $W_2(NMe_2)_6$ and excess Pr^iOH has been carried out in sealed vessels and the gaseous products have been analyzed. In addition to the expected dimethylamine, small quantities of molecular hydrogen have been detected. The reaction has also been carried out in sealed nmr tubes and the course of the reaction monitored by nmr spectroscopy as a function of time. In this manner, we observed an initial rapid alcoholysis followed by a slow build-up of the hydrido compound, along with other as yet uncharacterized compounds.

The detailed pathway leading to $W_4(\mu-H)_2(OPr^i)_{14}$ is thus not known at this time, but the experimental evidence is at least consistent with the view that the reaction proceeds by three distinct steps as shown in equations 2a, 2b and 2c below. The first step of the reaction, 2a, is an

2a $\qquad W_2(NMe_2)_6 + Pr^iOH(excess) \rightarrow W_2(OPr^i)_6 + 6\ HNMe_2$
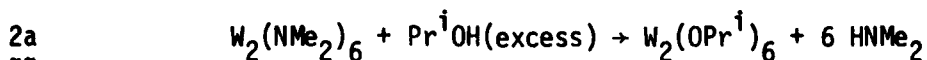
alcoholysis reaction and is common to all transition metal dimethylamides.[6] For molybdenum, the reaction stops here, yielding the well characterized compound $Mo_2(OPr^i)_6$ (M≡M).[3] For tungsten, the $W_2(OPr^i)_6$ formed in 2a will be solvated either by $HNMe_2$ or, more likely, Pr^iOH since the latter is present in excess. The previous characterization of $W_2(OPr^i)_6(py)_2$ substantiates this view.[2]

Step 2b represents the oxidative addition of H and Pr^iO across the tungsten-tungsten triple bond to give a solvated $W_2(\mu-H)(OPr^i)_7$ species. Solvation again probably involves coordination of excess iso-propanol

2b $W_2(OPr^i)_6 + Pr^iOH \rightarrow W_2(\mu\text{-}H)(OPr^i)_7$
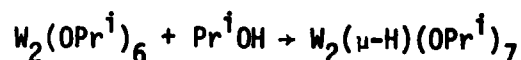
and there is direct evidence that $W_4(\mu\text{-}H)_2(OPr^i)_{14}$ forms dinuclear fragments in the presence of donor molecules such as pyridine, dioxane and isopropanol (see later).   Nothing can be said about the detailed mechanism of this RO-H addition across the M≡M bond. The source of the bridging hydride has been reliably established as coming from the hydroxyl group by reactions involving Pr^iOD and Pr^iOT. A mixture of Pr^iOH and Pr^iOT yields a $W_4(\mu\text{-}H/T)_2(OPr^i)_{14}$ product with only <u>ca</u>. 40% of the statistically possible tritiated product based on the known tritium enrichment in the isopropanol. On thermodynamic grounds, one would expect that the equilibrium position of reaction 3 would favor $W_2(\mu\text{-}H)$ and Pr^iOT.[7] However, in view of the fact that the compounds

3 $Pr^iOT + W_2(\mu\text{-}H) \rightleftharpoons Pr^iOH + W_2(\mu\text{-}T)$
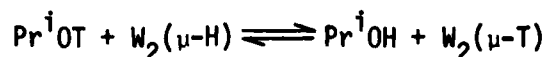
$W_4(\mu\text{-}H)_2(OPr^i)_{14}$ and $W_4(\mu\text{-}D)_2(OPr^i)_{14}$ do not react with Pr^iOD and Pr^iOH, respectively, to give H/D scrambling of the bridging hydride, the aforementioned observation quite probably represents a kinetic isotope effect associated with the relative rates of oxidative-addition of $Pr^iO\text{-}H$ and $Pr^iO\text{-}T$ across the W≡W bond. Finally, it should be noted that related additions to dinuclear compounds have been recently reported in which the metal-metal bond order is changed.[8]

The last step, 2c, in the formation of $W_4(\mu\text{-}H)_2(OPr^i)_{14}$ represents the dimerization of two unsolvated $W_2(\mu\text{-}H)(OPr^i)_7$ species. A Lewis base solvent molecule is replaced by an alkoxide bridge, a reaction which is common in the chemistry of polynuclear metal alkoxides.[9] This will take place upon stripping

2c
$$2 \ W_2(\mu\text{-H})(OPr^i)_7 \rightarrow W_4(\mu\text{-H})_2(OPr^i)_{14}$$
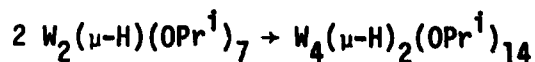
the excess isopropanol and dimethylamine and is merely the reverse of what is observed when $W_4(\mu\text{-H})_2(OPr^i)_{14}$ is dissolved in a donor solvent such as dioxane or pyridine.

Solid State Structure and Remarks on Bonding. The unit cell contains one molecule and in the space group $P\bar{1}$, this has a crystallographically imposed center of inversion. The positional and thermal parameters for the atoms constituting the molecule are given in Table 1. Interatomic distances and bond angles are given in Tables 2 and 3, respectively. An ORTEP drawing of the molecule (excluding hydrogen atoms), in which the atom numbering scheme is defined, is shown in Figure 1. A view of the $W_4(\mu\text{-H})_2O_{14}$ skeleton of the molecule is shown in Figure 2; this emphasizes the local distorted octahedral geometry about each tungsten atom.

The molecule consists of two $W_2(\mu\text{-H})(OPr^i)_7$ units linked by a pair of alkoxy bridges. With a W(1)-W(1)' distance of 3.407(1) Å, there is no reason to invoke the existence of a tungsten-to-tungsten bond between the two halves of the molecule. This M-M distance is very similar to that found in $[Mo(OPr^i)_3NO]_2$ (Mo-to-Mo = 3.324 Å)[10] which on electronic grounds should not have a molybdenum-to-molybdenum bond and is markedly different from the Mo-to-Mo distances observed in $Mo_2(OPr^i)_8$[11] (2.52 Å) and $Mo_2Cl_4(OPr^i)_6$[12] (2.73 Å) which have Mo-to-Mo double and single bonds, respectively. All three of the aforementioned molybdenum compounds contain a central $Mo_2(\mu\text{-}OPr^i)_2$ moiety and have planar M_2O_2 groups of the type observed here for W(1)W(1)'-(O7)(O7)'. In a series of trinuclear tungsten (IV) compounds where there are W-W single bonds, the W-W distances are in the range 2.74-2.77 Å.[13] The other tungsten-to-tungsten distance of 2.446(1) Å, for W(1) to W(2),

on the other hand, is quite consistent with the presence of a W=W bond.[14] Since the average oxidation number of tungsten is +4 in this molecule, there are eight tungsten electrons available for metal-to-metal bonding in this tetranuclear complex. The observed structure implies that these are utilized in the formation of two localized W=W bonds.

Since the outer tungsten atoms, W(2) and W(2)' are coordinated to three terminal and two bridging OPr^i ligands and the inner tungsten atoms, W(1) and W(1)', are coordinated to one terminal and four bridging OPr^i ligands and both inner and outer tungsten atoms are coordinated to one bridging hydrogen atom, there is a formal oxidation state difference between the two types of tungsten atoms: W(1) = +3½ and W(2) = +4½. It is, therefore, particularly interesting to note that the bridging hydrogen atom is closer to W(1), W(1)-H = 1.61(8) Å, than to W(2), W(2)-H = 1.89(8) Å. This may help minimize the imbalance of electron density distribution between the two types of tungsten atoms; if the H atom belonged entirely to W(1), each metal atom would have an oxidation state of +4.

It may also be noted that the W-O distances of groups _trans_ to the W-H bond are significantly longer than those which are _trans_ to W-OPr^i groups. This is entirely consistent with the well documented high _trans_-influence of the hydride ligand[15] and bears a striking parallel to the details of the structure of the $Mo_2Cl_8H^{3-}$ ion.[16]

Physico-Chemical Properties. Though $W_4(\mu\text{-H})_2(OPr^i)_{14}$ is black, there are no well defined absorption bands in the visible region of the spectrum. The black color arises from intense absorption in the u.v. region tailing into the visible region of the spectrum and small thin crystals appear orange.

$W_4(\mu-H)_2(OPr^i)_{14}$ is not thermally stable and decomposes above 75°C

in vacuo yielding isopropanol and propylene and as yet uncharacterized

tungsten containing residues. A weak molecular ion, $W_4(\mu-H)_2(OPr^i)_{14}^+$ was

detected in the mass spectrum, but the most significant ion with high m/e

value was that corresponding to $W_2(\mu-H)(OPr^i)_7^+$. When the field ionization

mode was used, this was the most intense ion in the spectrum. These results

are in full accord with the view that the tetranuclear complex consists of

two $W_2(\mu-H)(OPr^i)_7$ units joined relatively weakly by a pair of alkoxy

bridges. However, a cryoscopic molecular weight determination in benzene

gave M = 1480 ± 80 which shows that in non-coordinating solvents, the

tetranuclear nature of the complex is largely or totally maintained. In

p-dioxane, however, the molecular weight was close to half the value found

in benzene, which suggests that the tetranuclear complexes are cleaved in

donor solvents to give a solvated $W_2(\mu-H)(OPr^i)_7$ species.

The ^1H nmr spectrum of $W_4(\mu-H)_2(OPr^i)_{14}$ in toluene-d_8 at ca. 25°C is shown in

Figure 3. The spectrum is unchanged in the temperature range -60° to +60°C;

below -60°C the signals broaden and splittings due to H-H coupling are lost.

Evidently the molecule is fluxional and the seven distinct isopropoxy

groups found in the solid state structure are rapidly exchanging in solution.

The tungsten hydride resonance at δ = 7.87 ppm shows satellites due to

coupling to ^{183}W which has I = $\frac{1}{2}$ and 14.4% natural abundance. The intensity

of the satellites indicates that the hydride sees two equivalent tungsten

atoms which is consistent with the view that the fluxional process rapidly

equilibrates inner and outer tungsten atoms and the $W_2(\mu-H)$ moiety remains

intact. The fluxional process does not involve catalysis by free

isopropanol, as shown later, but beyond this we cannot say anything definitive about the mechanism. It may be noted, however, that the fluxional nature of this compound is quite in line with current knowledge of metal alkoxide chemistry. For example, a succession of bridge-for-terminal OPr^i exchanges could readily lead to the formation of the isomer shown below. Here the two tungsten atoms of one $W_2(\mu-H)$ unit are equivalent.
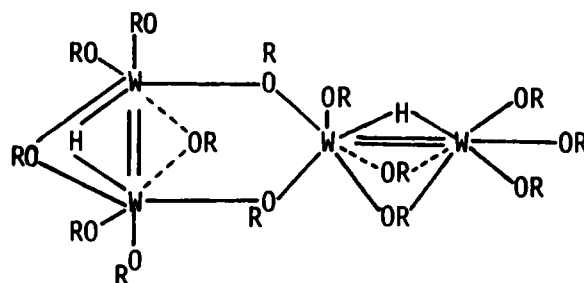
Thus, by simple bridge $\rightleftharpoons$ terminal OPr^i exchange processes, the $W_4(\mu-H)_2$-$(OPr^i)_{14}$ molecule could turn itself inside out and scramble all the OPr^i ligands and the two types of tungsten atoms without disruption of the $W_2(\mu-H)$ units: the hydrogen nuclei see two, not four, equivalent tungsten - 183 nuclei.

Reactivity of the Hydride Ligand

A quick survey of the type of reactivity associated with the bridging hydride ligand has been carried out by a series of nmr tube experiments.

With Pyridine. Addition of pyridine-d_5 to a solution of $W_4(\mu-H)_2(OPr^i)_{14}$ in toluene-d_8 causes a downfield shift of the hydride resonance; $\delta = 8.70$ ppm. Significantly, however, we do not observe any elimination of Pr^iOH and

formation of the previously characterized compound $W_2(OPr^i)_6(py)_2$. Evidently, the oxidative-addition step, 2b, is not reversible.

With Isopropanol. Additions of isopropanol and Pr^iOD (separate experiments) to a toluene-d_8 solution of $W_4(\mu-H)_2(OPr^i)_{14}$ reveal that the hydride ligand does __not__ exchange with the hydroxyl hydrogen atom of the free alcohol. Again, there is a shift of the hydride resonance to lower field, $\delta = 9.82$ ppm, in the presence of __excess__ Pr^iOH and we believe that this is associated with the presence of the solvated $W_2(\mu-H)(OPr^i)_7$ species which is formed in donor solvents.

With Tertiary Phosphines. Addition of triphenylphosphine and dimethylphenyl-phosphine to solutions of $W_4(\mu-H)_2(OPr^i)_{14}$ in toluene-d_8 yield dark red solutions,[17] but ^{1}H and ^{31}P nmr spectroscopy provided no indication of adduct formation.

With Unsaturated Hydrocarbons. Addition of ethylene, diphenylacetylene and allene to toluene-d_8 solutions of $W_4(\mu-H)_2(OPr^i)_{14}$, in separate experiments, caused a virtually instantaneous loss of the hydride resonance. Addition of a large excess of $CD_2=CH_2$ in a similar experiment was monitored by ^{2}H nmr spectroscopy: the labels in the excess ethylene were completely scrambled. Addition of 1-butene showed no reaction at room temperature over 2 days, but at +60°C isomerization to cis-2-butene occurred without any significant loss of the hydride resonance.

Though none of the tungsten containing products have been characterized in the above reactions, these observations support the view that $W_4(\mu-H)_2(OPr^i)_{14}$ is coordinatively unsaturated and can react with unsaturated hydrocarbons to give products of hydride insertion. With olefins, the insertion reaction is

apparently reversible and the position of equilibrium dependent of the nature of the olefin.

Further studies on this remarkable molecule are planned.

Preparation of $W_4(\mu\text{-D})_2(OPr^i)_{14}$

$W_4(\mu\text{-D})_2(OPr^i)_{14}$ was prepared in an analogous manner to that described for $W_4(\mu\text{-H})_2(OPr^i)_{14}$, except that Pr^iOD was used in place of Pr^iOH. The reaction time required to yield crystals was longer (perhaps because of the slower oxidation step involving $Pr^iO\text{-}D$ relative to $Pr^iO\text{-}H$).[21] [2]H nmr spectra recorded at 33.77 MHz, +16°C from toluene solution showed $\delta(W_2(\mu\text{-D}))$ at 7.90 ppm with $J_{183W\text{-}2H} = 16$ Hz.[22] The infrared spectrum was virtually identical to that of $W_4(\mu\text{-H})_2(OPr^i)_{14}$ given above; an unequivocal assignment of $\nu(W\text{-}H\text{-}W)$ and $\nu(W\text{-}D\text{-}W)$ is not possible.

Preparation of Tritium Enriched $W_4(\mu\text{-H})_2(OPr^i)_{14}$[23]

T_2O (10^{-2} mL, 10 MCi/mL) was added to dry degassed Pr^iOH in a 5 mL round bottomed flask. The solution was then stored over a small quantity of dried and degassed molecular sieves.

$W_2(NMe_2)_6$ (551 mg, 0.887 mmol) was dissolved in benzene (16.5 ml) in a 50 mL round bottomed flask and then frozen at liquid nitrogen temperature. The tritium enriched isopropanol was then added using a vacuum manifold. When the addition was complete, the flask containing $W_2(NMe_2)_6$, benzene and isopropanol was allowed to warm to room temperature. The solution turned from pale-yellow to brown and was stirred using a magnetic stirrer-spin bar, for 2 days at room temperature. The solvent was then stripped and the black solids dissolved in hexane (30 mL), filtered through a course frit, and the filtrate was set aside at room temperature for 3 days. No crystals formed so the volume of solvent was reduced to 20 mL and the flask was placed in the refrigerator at ca. 5°C. After 3 days, small crystals had formed;

Experimental Section

General procedures and the preparation of $W_2(NMe_2)_6$ have been described previously.[18]   Dry and oxygen-free solvents were used at all times.

^1H and ^2H nmr spectra were recorded on Varian XL 100 and HR 220 spectrometers. Infrared spectra were obtained from nujol mulls between CsI plates using a Perkin Elmer 273 spectrometer. Mass spectra were obtained by the method of direct insertion using AEI MS902[19] and Varian MAT 371[20] mass spectrometers. Elemental analyses were obtained from the Alfred Bernhardt Microanalytical Laboratories, West Germany.

Preparation of $W_4(\mu-H)_2(OPr^i)_{14}$

$W_2(NMe_2)_6$ (2.95 g, 4.67 mmol) was dissolved in toluene (40 mL). To this solution, isopropanol (15 mL) was added: the color turned from pale yellow to dark brown. The solution was stirred at room temperature for 6 h. The solvent was stripped and the black solids dissolved in n-hexane (25 mL). The solution was warmed to ca. 40°C and then allowed to cool slowly to -15°C. After 24 h, black crystals of $W_4(\mu-H)_2(OPr^i)_{14}$ (1.5 g, 46% yield based on tungsten) were collected by filtration and dried in vacuo. Anal. calcd. for $W_4O_{14}C_{42}H_{100}$: C, 32.2; H, 6.44. Found: C, 32.0; 6.16%. I.r. data in the range 1400-200 cm^{-1}: 1378 s, 1368 s sh, 1320 m, 1262 m, 1165 m, 1110 s (broad), 1020 w, 997 m, 975 to 960 s (broad), 940 m sh, 845 s, 835 m, 820 m, 800 m, 720 w, 610 s, 590 s, 475 m, 460 w, 410 w, 372 w, 300 w (broad). ^1H nmr data obtained at 220 MHz, +16°C from a toluene-d_8 solution: $\delta(W_2(\mu-H)) = 7.87$, $J_{183W-1H} = 96$ Hz; $\delta(CH) = 4.87$, $J_{HH} = 6$ Hz; $\delta(CH_3) = 1.29$, $J_{HH} = 6$ Hz. δ in ppm downfield of Me_4Si.

the flask was then placed in the freezer compartment of the refrigerator (-15°C) and was left there for 10 days to promote further crystallization. Subsequent filtration yielded ca. 50 mg of tritium enriched $W_4(\mu-H)_2(OPr^i)_{14}$ which was dried in vacuo.

The level of tritium enrichment was determined by scintillation counting using a Beckman LS-250. The fluors 1,4-bis-2-(5-phenyloxazolyl)-benzene (0.1 g) and 2,5-diphenyloxazole (1 g) dissolved in toluene (200 mL) provided a standard fluorescent solution for the detection of tritium. The intense brown color of toluene solutions of $W_4(\mu-H)_2(OPr^i)_{14}$ reduced the counting efficiency because of color quenching. Consequently, blank experiments were carried out involving toluene solutions of unlabelled $W_4(\mu-H)_2(OPr^i)_{14}$, the fluor-toluene solution and either tritium enriched H_2O or ecdysterone (randomly labelled). In this way, it was possible to determine the level of tritium enrichment in the $W_4(\mu-H/T)_2(OPr^i)_{14}$ prepared above. These results indicated 0.8 ± 0.1T per W_4-unit, i.e. only ca. 40% of the statistical tritium enrichment was achieved based on the level of tritium enrichment of the isopropanol.

Collection of X-Ray Data. The triclinic crystal employed for data collection was bounded by the ±(100), ±(010), and ±(001) faces at separations of 0.19, 0.15, and 0.54 mm, respectively. The crystal was sealed in a 0.7 mm glass capillary with the long crystal axis at an angle of ca. 45° to phi. The capillary walls made accurate measurements of the dimensions of the crystal faces difficult.

The crystal was shown to be of good quality from ω-scans of several intense reflections which had peak widths at half height of less than 0.18°. Preliminary lattice constants and the orientation matrix used for data

collection were obtained from least squares refinement of the diffractometer settings of 15 intense reflections in the range $4.4° < 2\theta MoK\alpha < 26.1°$, $\lambda(MoK\alpha) = 0.71073$ Å. Final lattice parameters were calculated similarly following data collection using 15 reflections having $20.0° < 2\theta MoK\alpha < 25.0°$ and chosen to give a good sampling of crystal indices. The final cell constants are: $a = 12.645(4)$ Å, $b = 13.157(4)$ Å, $c = 9.788(3)$ Å, $\alpha = 102.43(2)°$, $\beta = 67.80(2)°$, $\gamma = 101.05(2)°$ and $V = 1461(1)$ Å^3. The observed volume is consistent with that anticipated for $Z = 1$, assuming four tungsten atoms in the molecule. The structure was solved in the centrosymmetric space group $P\bar{1}$.

Data were collected at $22\pm2°C$ using a Syntex $P\bar{1}$ autodiffractometer, with graphite monochromatized $MoK\alpha$ radiation and the $\theta-2\theta$ scan technique using scan rates varying from $4°$ to $24°$ per min, depending upon the intensity of the reflection. The scans ranged from $MoK\alpha_1 - 1.0°$ to $MoK\alpha_2 + 1.0°$. A total of 3782 unique data having $0° < 2\theta MoK\alpha < 45.0°$ were measured, of which those 2949 having $I > 3\sigma(I)$ were used in subsequent least squares refinement. The intensities of three standard reflections measured every 97 data points showed a decrease of 16.7% over the period of data collection. The data set was corrected for this decomposition. After corrections for Lorentz and polarization effects, the intensities were reduced to a set of relative $|F_o|^2$ values for use in structure refinement.

Solution and Refinement of the Structure.[24] The positions of the two independent tungsten atoms were obtained from a three dimensional Patterson map and their atomic coordinates were refined by least squares to give the following discrepancy indices:

$$R_1 = \Sigma ||F_o|-|F_c||/\Sigma|F_o| = 0.165$$

$$R_2 = \Sigma w(|F_o|-|F_c|)/\Sigma w|F_o|^2]^{1/2} = 0.232$$

The function minimized in least squares refinement was $\Sigma w(|F_o|-|F_c|)^2$, where the weighting factor, w, equals $4F_o^2/\sigma(F_o^2)^2$. A value of 0.07 was used for the parameter p in the weighting function.[25] The atomic scattering factors used were those of Cromer and Waber.[26] Anomalous dispersion effects[27] were included in the calculated scattering factors. A difference Fourier synthesis at this point revealed the positions of 24 nonhydrogen atoms belonging to 6 independent ligands. Refinement of the positional and isotropic thermal parameters of these atoms, followed by a second difference Fourier synthesis revealed the positions of the atoms of the seventh ligand. The positional and isotropic thermal parameters of the 30 nonhydrogen atoms were refined to yield discrepancy indices $R_1 = 0.097$ and $R_2 = 0.117$. At this point, an absorption correction was applied to the data since $\mu = 83.6$ cm^{-1}. The maximum, minimum, and average transmission coefficients were 0.351, 0.181 and 0.302, respectively. Refinement was then continued employing isotropic thermal paramters, to yield $R_1 = 0.057$ and $R_2 = 0.075$.

Examination of a difference Fourier map suggested that the isopropyl group attached to O(4) was disordered. A two-fold disorder about the O(4)-C(41) bond was indicated. It was assumed that four methyl groups (C(42), C(43), C(44), C(45)), each having an occupation number of 0.5, were bonded to C(41). Inspection of the C(41) to methyl bond lengths indicated that C(41) might itself be slightly disordered. However, since the displacement was slight (~0.2 Å) it was ignored. All atoms were now

refined to convergence utilizing anisotropic thermal parameters for the tungsten and oxygen atoms and isotropic thermal parameters for the carbon atoms. The residuals at this point were $R_1 = 0.037$, $R_2 = 0.052$ and the esd of an observation of unit weight was 1.25.

Since extra-crystallographic considerations had led us to consider the possible presence of hydrogen atoms in bridging positions, we now made an effort to find and refine them. A weak peak lying near the "empty" bridging position between $W(1)$ and $W(2)$ was introduced as a hydrogen atom and refinement was continued to a new convergence. The hydrogen atom behaved quite well in refinement and the final figures of merit were $R_1 = 0.033$, $R_2 = 0.045$, esd = 1.10 and no parameter shifted by more than 0.1 times its esd in the last cycle.

References and Footnotes

1. (a) Princeton University, (b) Indiana University, (c) Texas A&M University.

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19. We thank Mr. Peter Cook of Queen Mary College, London University, for obtaining mass spect by electron impact.

20. We thank Drs. Bruce Calvert and J. Carter Cook, of the School of Chemical Sciences, Illinois University, for obtaining mass spectra using the field ionization method.

21. The formation of $Mo_2(\mu-D)Cl_8^{3-}$, which involves DCl addition, is slower than the formation of $Mo_2(\mu-H)Cl_8^{3-}$ by addition of HCl to $Mo_2(OAc)_4$. See discussion in ref. 8b.

22. As expected since $\gamma(^2H) = 4.107 \times 10^3$ radians/(S.G.).

23. We thank Professor Charles Gilvarg, Department of Biochemistry, Princeton University, for his assistance and guidance in the use of tritium labelled compounds.

24. Computer programs used in data reduction, structural solution and refinement were those of the Enraf-Nonius structure determination package. The software package was used on a PDP 11/45 computer at the Molecular Structure Corporation, College Station, Texas.

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Table 1. POSITIONAL AND THERMAL PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS.[a]

ATOM	X	Y	Z	B(1,1)	B(2,2)	B(3,3)	B(1,2)	B(1,3)	B(2,3)
1)	0.06187(3)	0.12708(3)	0.50468(4)	1.79(1)	2.37(2)	2.20(1)	0.10(1)	-0.53(1)	0.34(1)
2)	0.24897(3)	0.23481(3)	0.45459(4)	2.12(1)	2.75(2)	2.61(1)	-0.30(1)	-0.72(1)	0.54(1)
1)	0.2717(6)	0.3799(6)	0.5313(8)	3.3(3)	3.5(3)	4.8(3)	-0.6(3)	-1.2(2)	1.1(3)
2)	0.3653(6)	0.2543(6)	0.2589(8)	3.2(3)	4.2(3)	3.3(3)	-1.2(3)	-0.2(2)	0.8(3)
3)	0.3350(5)	0.1957(6)	0.5493(7)	3.0(2)	4.5(3)	4.3(3)	0.5(2)	-2.0(2)	-0.1(3)
4)	0.1174(6)	0.2508(6)	0.3795(7)	3.6(2)	3.6(3)	3.4(2)	0.3(2)	-1.7(2)	0.5(2)
5)	0.2935(6)	0.0855(5)	0.3489(7)	2.2(2)	3.7(3)	3.9(7)	-0.1(2)	-1.2(2)	0.5(2)
6)	-0.0795(6)	0.1822(5)	0.6230(8)	2.2(2)	2.9(3)	4.6(3)	0.5(2)	-0.2(2)	-0.0(3)
7)	0.0260(6)	0.1016(6)	0.6117(6)	2.5(2)	3.2(3)	2.5(2)	-0.1(2)	-1.2(2)	0.8(2)
11)	0.2040(11)	0.4495(10)	0.656(2)	5.2(6)	5.7(5)	6.3(8)	1.1(4)	-1.1(5)	-1.1(5)
12)	0.2937(12)	0.5006(12)	0.628(2)	8.3(6)	3.9(7)	9.1(8)	-0.6(6)	-3.2(6)	-0.2(6)
13)	0.2073(15)	0.4718(15)	0.803(2)	9.8(9)	6.5(8)	4.2(5)	0.1(8)	-1.2(6)	-1.0(6)
21)	0.4089(12)	0.3340(11)	0.251(1)	4.6(6)	5.0(7)	4.7(5)	-2.2(5)	-0.3(5)	1.7(5)
22)	0.5572(14)	0.3371(17)	0.102(2)	5.2(8)	12(1)	8(1)	-3.6(8)	2.9(7)	-2(1)
23)	0.4807(15)	0.4519(14)	0.195(2)	8.0(9)	7.7(9)	11(1)	-2.0(8)	-1.9(8)	4.8(7)
31)	0.4423(9)	0.2404(12)	0.577(1)	3.2(4)	6.9(7)	5.2(6)	-0.5(4)	-4.1(3)	1.1(6)
32)	0.5384(11)	0.1776(16)	0.465(2)	3.2(5)	13(1)	12(1)	1.8(6)	-2.7(5)	1(1)
33)	0.4188(12)	0.2568(20)	0.739(2)	6.0(6)	21(2)	6.2(6)	1.6(8)	-4.1(4)	2.1(8)
41)	0.0916(12)	0.2919(11)	0.277(2)	12.0(6)	7.7(6)	13.9(6)	-1.2(5)	-9.4(4)	6.5(4)
51)	0.2591(9)	0.0089(9)	0.218(1)	3.3(4)	3.5(5)	2.0(4)	0.4(4)	0.1(3)	-0.7(4)
52)	0.3769(10)	-0.0106(11)	0.216(2)	3.7(5)	6.9(7)	6.1(7)	3.4(4)	0.0(5)	-0.3(6)
53)	0.2694(11)	0.0443(11)	0.074(1)	5.2(6)	6.5(7)	2.9(4)	0.5(5)	-0.7(4)	-0.0(5)
61)	-0.1071(10)	0.2841(9)	0.703(1)	3.5(5)	3.3(5)	6.4(7)	0.0(4)	0.4(5)	0.4(5)
62)	-0.1155(12)	0.2908(12)	0.872(2)	7.5(7)	6.7(8)	5.5(6)	2.8(6)	-1.7(5)	-2.7(6)
63)	-0.2189(10)	0.3019(10)	0.692(2)	4.0(4)	5.7(6)	9.9(8)	3.2(4)	-1.5(5)	0.9(5)
71)	0.0703(11)	-0.0159(9)	0.721(1)	3.4(4)	5.6(5)	2.3(3)	-0.3(4)	-1.2(3)	1.2(3)
72)	0.0657(10)	0.0808(11)	0.843(1)	5.8(5)	5.3(6)	4.4(4)	-0.9(5)	-3.1(3)	0.5(4)
73)	0.1940(9)	-0.0457(11)	0.638(1)	3.8(4)	6.3(6)	8.5(6)	1.5(4)	-3.3(3)	1.1(5)

42)[b]	0.133(2)	0.269(3)	0.134(3)	6.8(7)
43)[b]	0.079(2)	0.416(2)	0.357(3)	5.0(5)
44)[b]	-0.007(3)	0.292(3)	0.265(3)	7.6(8)
45)[b]	0.191(3)	0.362(4)	0.180(5)	10.9(12)
1)	0.103(6)	0.227(6)	0.608(7)	1.(2)

[a] The form of the anisotropic thermal parameter is:

$$\exp[-1/4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)].$$

[b] These methyl group carbons refined at 0.5 occupancy.

Table 2. Bond Distances, Angstroms[a]

Bond	Distance	Bond	Distance
W(1)-W(1)'	3.4C7(1)	C(3,1)-O(3)	1.46(2)
-W(2)	2.446(1)	-C(3,2)	1.53(2)
-O(4)	2.101(7)	-C(3,3)	1.51(2)
-O(5)	2.005(7)	C(4,1)-O(4)	1.40(2)
-O(6)	1.897(6)	-C(4,2)	1.28(4)
-O(7)	2.038(6)	-C(4,3)	1.67(3)
-O(7)'	2.187(6)	-C(4,4)	1.29(4)
W(2)-O(1)	1.904(8)	-C(4,5)	1.54(5)
-O(2)	1.959(7)	C(5,1)-O(5)	1.44(1)
-O(3)	1.892(7)	-C(5,2)	1.55(2)
-O(4)	2.116(7)	-C(5,3)	1.53(2)
-O(5)	2.100(7)	C(6,1)-O(6)	1.44(1)
C(1,1)-O(1)	1.44(2)	-C(6,2)	1.60(2)
-C(1,2)	1.51(2)	-C(6,3)	1.52(2)
-C(1,3)	1.53(2)	C(7,1)-O(7)	1.45(1)
C(2,1)-O(2)	1.40(1)	-C(7,2)	1.54(2)
-C(2,2)	1.52(2)	-C(7,3)	1.55(2)
-C(2,3)	1.55(3)	W(1)-H	1.61(8)
		W(2)-H	1.89(8)

[a] Atoms are labelled as in Figure 1. Numbers in parentheses are the estimated standard deviations in the least significant figures.

Table 3. Bond Angles, Degrees[a]

Atoms	Angle	Atoms	Angle
W(1)-W(1)'-W(2)'	142.05(2)	W(1)-O(5)-W(2)	73.1(2)
-O(4)	142.0(2)	W(1)-O(7)-W(1)'	107.5(3)
-O(5)	90.9(2)	W(2)-O(1)-C(1,1)	134.3(7)
-O(6)	94.0(2)	W(2)-O(2)-C(2,1)	125.9(7)
-O(7)	37.8(2)	W(2)-O(3)-C(3,1)	133.2(8)
-O(7)'	34.8(2)	W(2)-O(4)-C(4,1)	145(1)
W(2)-W(1)-O(4)	54.8(2)	W(2)-O(5)-C(5,1)	140.5(6)
-O(5)	55.2(2)	W(1)-O(4)-C(4,1)	142.2(9)
-O(6)	122.6(2)	W(1)-O(5)-C(5,1)	144.8(6)
-O(7)	120.6(2)	W(1)-O(6)-C(6,1)	133.9(7)
-O(7)'	139.0(2)	W(1)-O(7)-C(7,1)	129.0(6)
W(1)-W(2)-O(1)	124.9(2)	W(1)'-O(7)-C(7,1)	121.1(6)
-O(2)	127.2(2)	O(1)-C(1,1)-C(1,2)	108(1)
-O(3)	110.4(2)	-C(1,3)	111(1)
-O(4)	54.3(2)	C(1,2)-C(1,1)-C(1,3)	112(1)
-O(5)	51.7(2)	O(2)-C(2,1)-C(2,2)	107(1)
O(4)-W(1)-O(5)	78.2(3)	-C(2,3)	113(1)
-O(6)	91.7(3)	C(2,2)-C(2,1)-C(2,3)	111(1)
-O(7)	173.4(3)	O(3)-C(3,1)-C(3,2)	107(1)
-O(7)'	107.6(3)	-C(3,3)	106(1)
O(5)-W(1)-O(6)	168.6(3)	C(3,2)-C(3,1)-C(3,3)	115(1)
-O(7)	95.2(3)	(4)-C(4,1)-C(4,2)	127(2)
-O(7)'	86.6(3)	-C(4,3)	102(2)
O(6)-W(1)-O(7)	95.0(3)	-C(4,4)	130(2)
-O(7)'	91.6(3)	-C(4,5)	115(2)
O(7)-W(1)-O(7)'	72.5(3)	C(4,2)-C(4,1)-C(4,3)	120(2)

Table 3 (Continued)

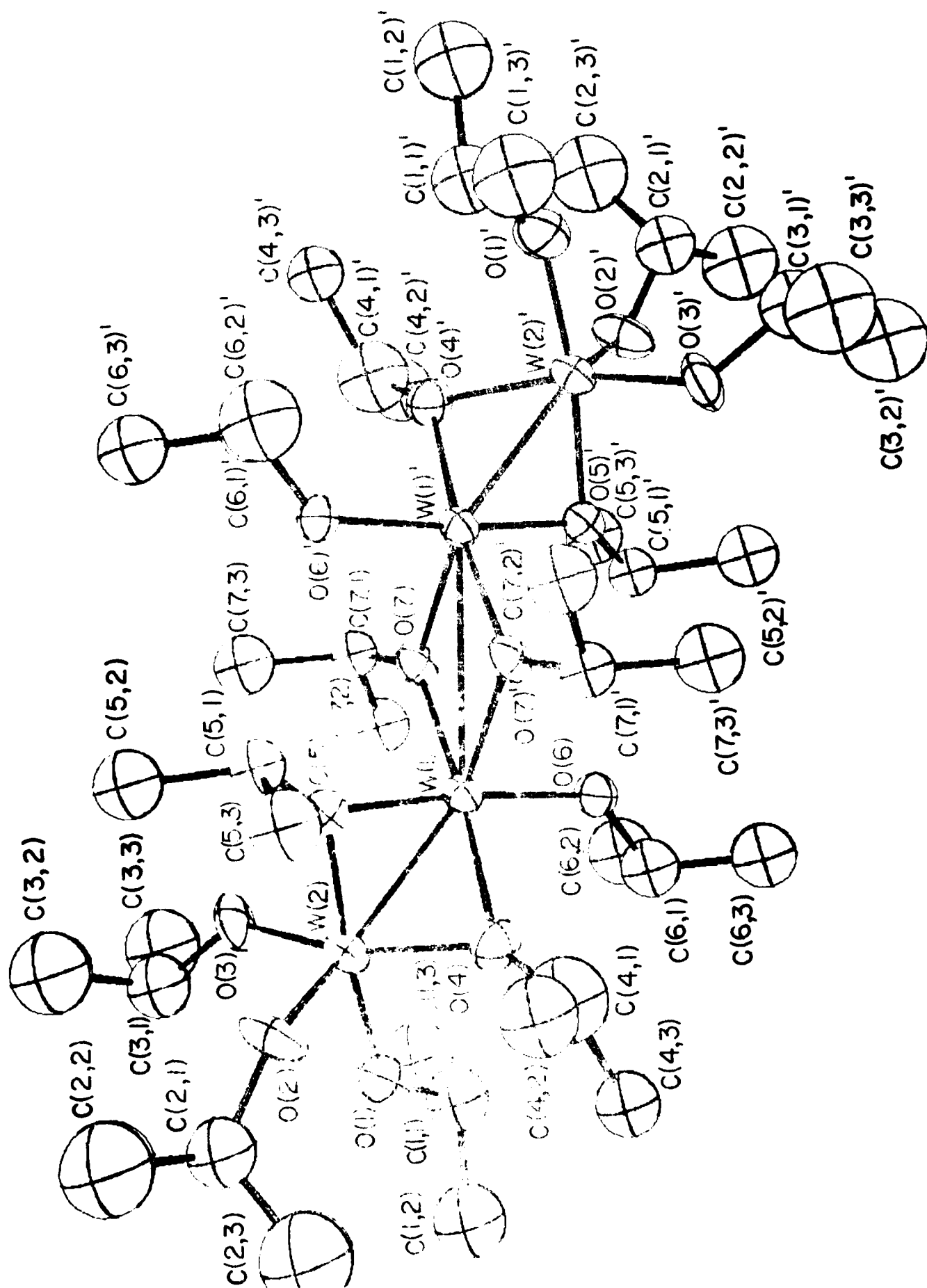| Atoms	Angle	Atoms	Angle
O(1)-W(2)-O(2)	91.9(3)	C(4,4)-C(4,1)-C(4,5)	114(3)
-O(3)	94.3(3)	O(5)-C(5,1)-C(5,2)	109(1)
-O(4)	94.5(3)	-C(5,3)	112(1)
-O(5)	169.9(3)	C(5,2)-C(5,1)-C(5,3)	112(1)
O(2)-W(2)-O(3)	101.7(4)	O(6)-C(6,1)-C(6,2)	109(1)
-O(4)	90.5(3)	-C(6,3)	109(1)
-O(5)	85.2(3)	C(6,2)-C(6,1)-C(6,3)	113(1)
O(3)-W(2)-O(4)	164.6(3)	O(7)-C(7,1)-C(7,2)	111(1)
-O(5)	95.8(3)	-C(7,3)	108(1)
O(4)-W(2)-O(5)	75.9(3)	C(7,2)-C(7,1)-C(7,3)	113(1)
W(1)-O(4)-W(2)	70.9(2)		
W(1)-H-W(2)	88(4)	O(7)'-W(1)-H	170(3)
W(1)-W(2)-H	41(3)	O(1)-W(2)-H	88(2)
W(2)-W(1)-H	51(3)	O(2)-W(2)-H	159(2)
O(4)-W(1)-H	74(3)	O(2)-W(2)-H	99(2)
O(5)-W(1)-H	104(3)	O(4)-W(2)-H	69(2)
O(6)-W(1)-H	78(3)	O(5)-W(2)-H	91(2)
O(7)-W(1)-H	107(3)		

[a]Atoms are labelled as in Figure 1. Numbers in parentheses are the
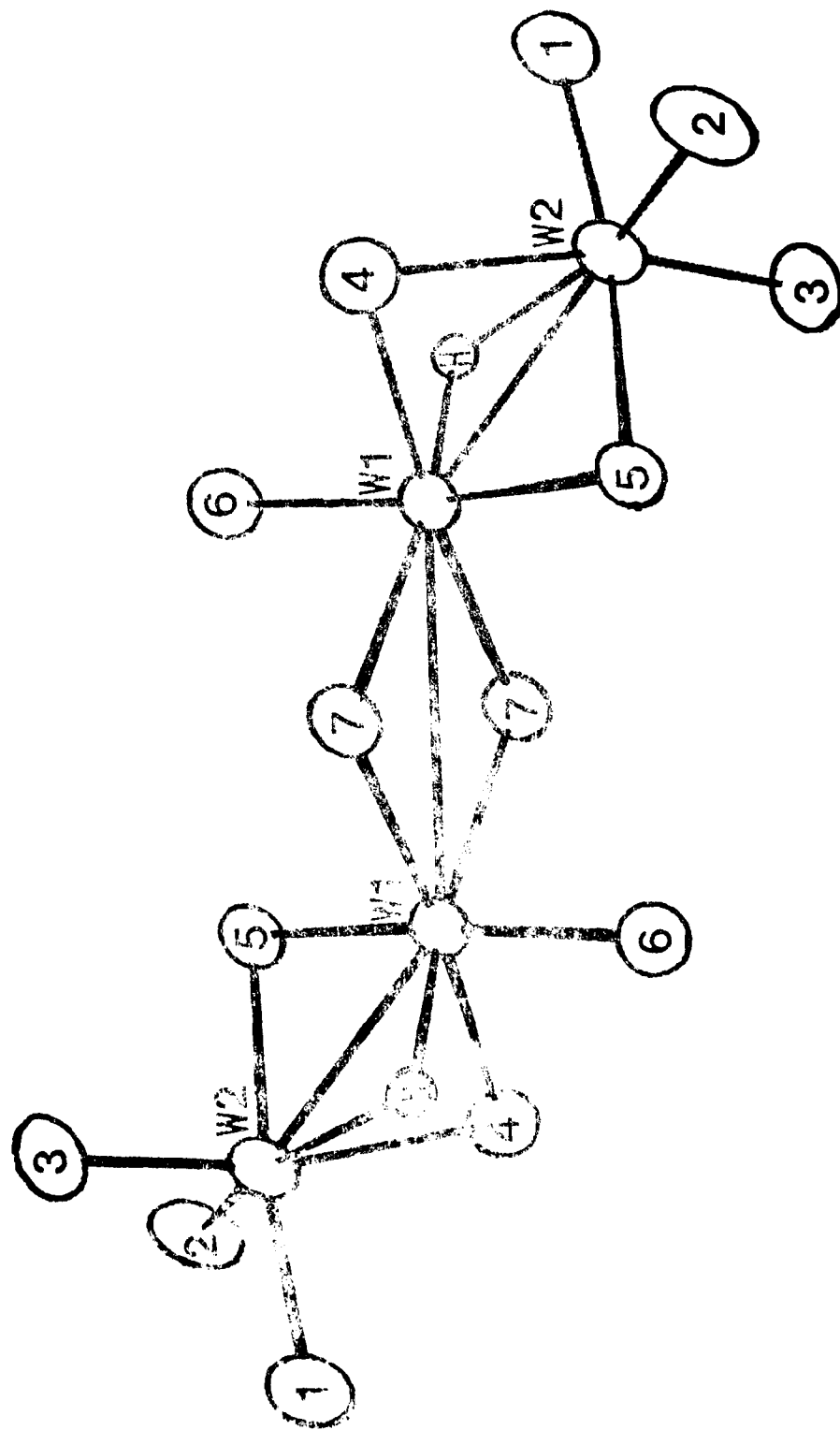estimated standard deviations in the least significant figures.

Captions to Figures

Fig. 1. An ORTEP view of the $W_4(\mu\text{-H})_2(OPr^i)_{14}$ molecule, omitting the μ-H atoms, and showing the atom numbering scheme used in Tables 2 and 3.

Fig. 2. A view of the $W_4(\mu\text{-H})_2{}^i{}_{14}$ skeleton, showing the bridging hydrogen atoms and emphasizing the essentially octahedral coordination of each tungsten atom.

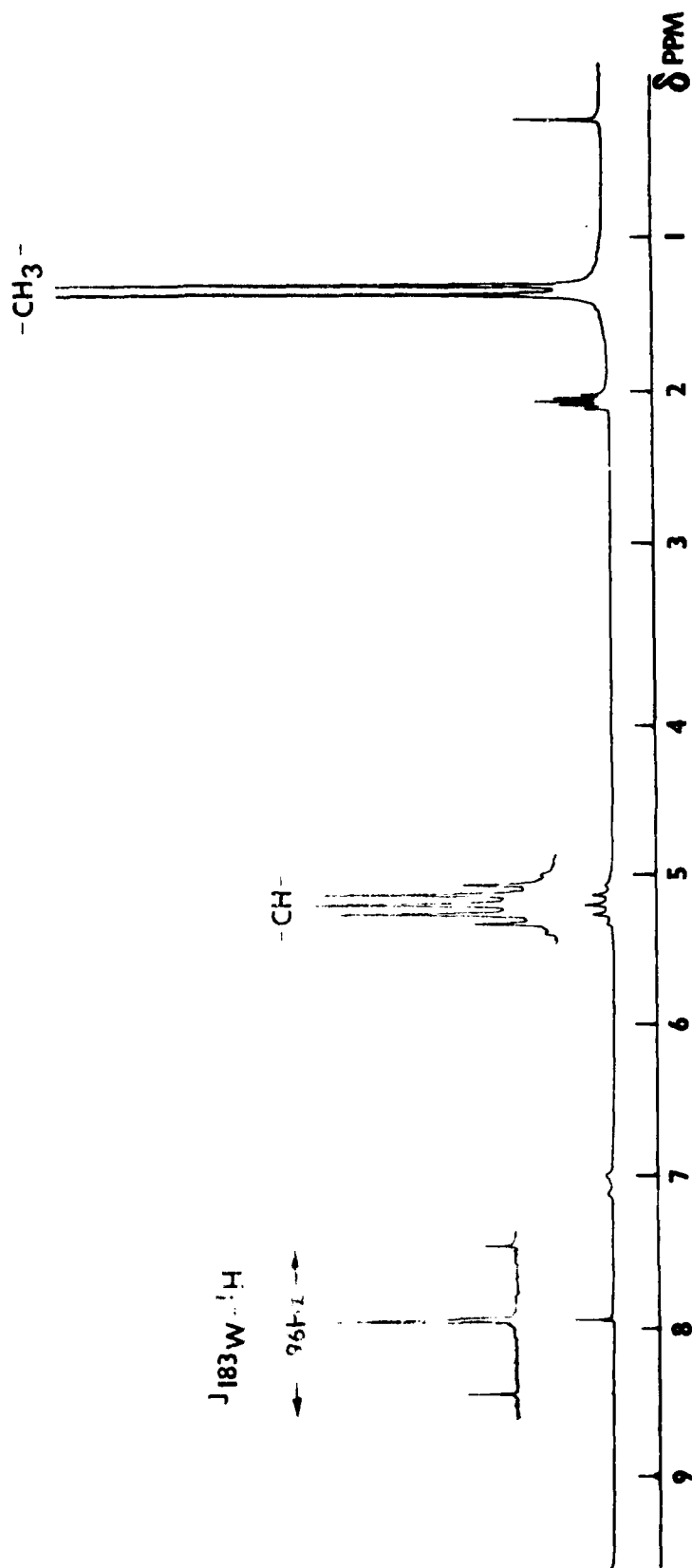**Fig. 3.** ^{1}H nmr spectrum of a toluene-d_8 solution of $W_4(\mu\text{-H})_2(OPr^i)_{14}$ recorded at 100 MHz, +25°C in the FT mode.

^{1}H

$W_4(O^iPr)_{14}(\mu-H_2)$

-CH$_3$ -

-CH-

$J_{183W^{-1}H}$
⟵ 96 ⟶

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